

Non-intrusive Optical Techniques for the Study of Pulverized Coal Particles during Devolatilization and Combustion*

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This paper will discuss applications of Fourier transform infrared (FT-IR) spectroscopy and laser spark spectroscopy (LSS) as in situ diagnostics for disperse phase combustion environments. The ultimate goal of the FT-IR work is the identification of gas phase species, and the determination of their temperature and concentration during the combustion of pulverized coal particles. We are developing LSS as a complementary technique for the in situ elemental analysis of coal, char, and ash particles in combustion environments.

Fourier transform spectroscopy

We have made infrared absorption measurements for sized coal particles entrained in a laminar flow reactor. The combustion is initiated by hot bath gases produced in a $H_2/O_2/N_2$ flat flame at the base of the reactor. The interface between the flow reactor and the FT-IR system is shown in Figure 1; detailed descriptions of the experimental apparatus and typical infrared absorption spectra have been given elsewhere (1).

FT-IR spectroscopy has been shown to be an effective technique for detection of many different species simultaneously over a wide spectral bandwidth when conditions permit time-averaged measurements along a line-of-sight (1,2). This past year has seen the extension of these measurements into the high resolution domain and the careful quantitation of the technique's ultimate sensitivity for several molecules.

Fast absorption measurements have been plagued by the infrared emission of hot coal particles passing through the detector field-of-view. These signals act as an additional noise source, and are mitigated only somewhat by laborious time-averaging. This has prevented the measurement of spectra at a resolution greater than 0.5 cm^{-1} . We have found, however, that this particle generated "noise" occurs at Fourier frequencies lower than the pertinent bandwidth containing infrared spectral information. Electronic filtering of the detector output has greatly reduced this particle noise, and allowed us to make the first reported measurements of pulverized coal combustion products at a spectral resolution of 0.08 cm^{-1} .

Although these measurements are more time consuming than those at lower resolution, they allow a more accurate determination of both the molecular rotational temperature and concentration. This is due principally to the lessened interference of nearby absorption lines from other species (mainly water) and higher excited state transitions. These measurements have also allowed us to observe that the measured line width of CO and CO_2 transitions is considerably greater than the reported values of 0.04 cm^{-1} at temperatures around 1300 K. Measured widths at half maximum are 0.105 cm^{-1} , and we postulate that the additional width is caused by collisional broadening with the copious quantity of water present (15 mol %). An example is shown in Figure 2 for a portion of the CO P-branch rotation-vibration band produced during the combustion of a pulverized western Kentucky bituminous coal. The CO rotational temperature determined from the relative intensities of the absorption lines was $1218 \pm 28\text{ K}$ and was in good agreement

with a temperature of 1247 \pm 22 K derived from the CO₂ ω_3 R-branch rotation-vibration during the same experimental measurement.

Reduction of the noise caused by particulate emission has increased our sensitivity for many small infrared-active molecules (CO, CH₄, NO, HCN, H₂S) to about 100 ppm at combustion temperatures in the presence of coal particles. Current efforts at detecting minor products of combustion in situ have been hampered by the low particle number density we have been able to entrain in our flow reactor (2 cm⁻³), and by the serious overlap of water absorption lines with N- and S-containing species of interest.

Concentration measurements were made by entraining known amounts of carbon dioxide and nitric oxide into the flow reactor. Using literature values of line strengths, the corresponding experimental intensities could be theoretically calculated for a variety of other molecular species in our FT-IR/flow reactor system. This approach is effective in minimizing uncertainties in absolute intensity measurements which arise from line-shape distortions caused by our instrument. In Figure 3 we show the measured concentration of CO and CO₂ at 38 msec residence for coal particles in the +30/-50 micrometer size range as a function of excess oxygen in the flow reactor.

Laser spark spectroscopy

We have developed the technique of laser breakdown spectroscopy for analyzing the composition of particles and droplets suspended in air (3). As such, this technique should prove invaluable as an in situ real-time diagnostic for application to fundamental studies of the combustion or gasification of coal, coal-derived liquids and coal-water slurries.

A high-power pulse was generated by a Nd:YAG laser and focused on individual coal particles carried in a gas flow. Absorbed energy was sufficient to completely vaporize the particles, and to cause avalanche breakdown of the vapor. The emission spectra from the plasma were analyzed to identify lines characteristic of the specific elements. Because of the strong continuum emission at early time of the spark, a time-gated optical multichannel analyzer was used to record the emission spectra. Timing and spectral windows were carefully selected to minimize the continuum emission, and to eliminate interference from nearby or overlapping lines from the atoms of interest. We succeeded in isolating spectral features of the major elements: carbon, nitrogen, oxygen, as well as hydrogen, sodium, and chlorine.

A two-color cross-beam laser technique was developed to provide a simultaneous trigger for the breakdown laser and a measurement of the size of the particle being analyzed. A schematic diagram of the experimental apparatus is shown in Figure 3. With this apparatus it is possible to correlate the emission spectrum and intensity with the particle size. In addition, detection limits of various species of interest were deduced from these cross-correlation measurements.

Laboratory experiments were conducted using pulverized bituminous coal particles and water droplets with added impurities. The latter experiments used a piezoelectric droplet generator for the purpose of creating a series of water particles of carefully controlled diameter. This greatly facilitates the calibration of spectral emission with such variables as the droplet size, atomic concentration, incident laser energy, and spectrometer response. An emission spectrum is shown in Figure 4 for the sodium 5890 Å line (grating resolution was not sufficient to resolve the doublet in this spectrum). This spectrum originated from the vaporization of a single water droplet 70 micrometers in diameter, containing 0.1% Na by weight.

REFERENCES

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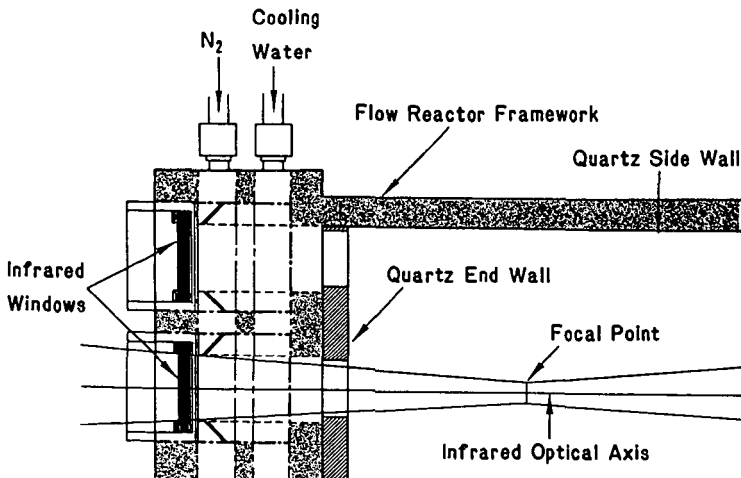
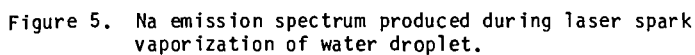
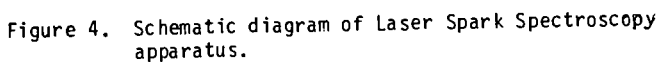


Figure 1. Schematic diagram of FT-IR / flow reactor interface.



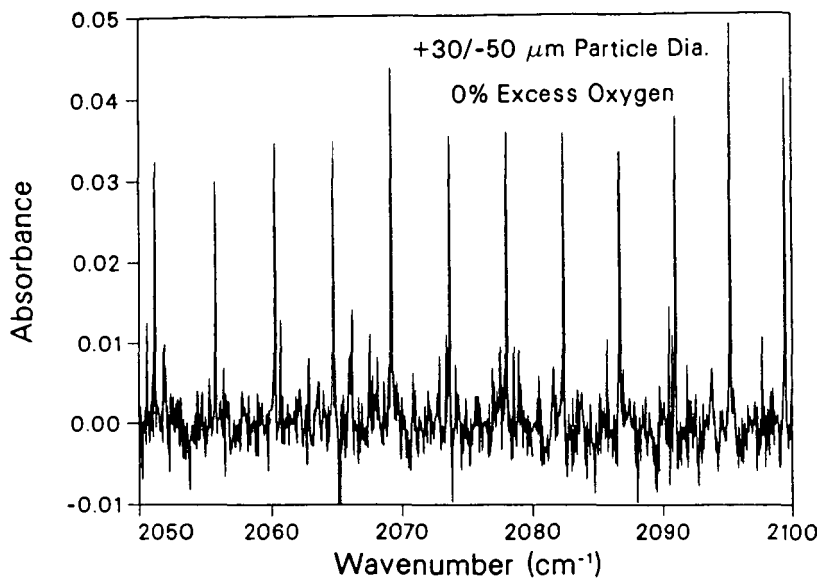


Figure 2. Absorbance spectrum of CO produced during pulverized coal combustion.

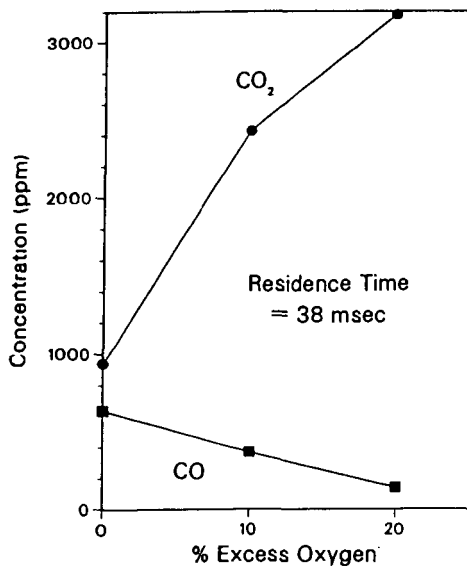


Figure 3. CO and CO₂ concentration in flow reactor as a function of excess oxygen.